PATENT SPECIFICATION

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PROVISIONAL SPECIFICATION

Improvements in the Manufacture of Ethers of Cellulose and Other Carbohydrates.

We, HORACE FINNINGLEY OXLEY, EDWARD BOADEN THOMAS and JOHN DOWNING, all subjects of the King of Great Britain, of the Works of British Celanese Limited, Spondon, near Derby, do hereby declare the nature of this invention to be as follows:—

This invention relates to improvements in the manufacture of cellulose derivatives and particularly to improvements in the manufacture of ethers of cellulose and other carbohydrates.

For certain purposes, for example for use in the manufacture of sizes, it is desirable that ethers of cellulose and other carbohydrates, for example starch, should not have too high a viscosity; and in order to produce ethers of the low viscosity required, it has been proposed either to subject the carbohydrate material to partial degradation before etherification, for example by heating it with acids or alkalis, or to carry out the etherification under such conditions as to cause degradation, for example by the use of high temperatures Both these methods, however have the disadvantage that it is not possible to be certain that the product eventually obtained will have exactly the desired viscosity.

It has now been discovered that the viscosity of ethers of carbohydrates may be reduced by subjecting the ethers themselves to a ripening operation in the presence of oxygen or other oxidising atmosphere and an alkali e.g. sodium and potassium hydroxides, tetra - methyl ammonium hydroxide and other strong organic bases. At ordinary temperatures the reduction in viscosity proceeds comparatively slowly, so that it is easy to take samples at suitable intervals and to interrupt the ripening process when a product of the desired degree of viscosity has been obtained.

The ripening operation is preferably carried out by allowing an ether which has been obtained e.g. by etherification of cellulose in the presence of alkali, to stand in a moist condition while it is still impregnated with alkali until the desired degree of viscosity is produced. Ethers produced in the absence of alkali, for example cellulose ethers obtained by etherifying cellulose with ethylene oxide without a catalyst or in the presence of an acid as catalyst, may be impregnated with alkali and then allowed to stand in a moist condition. Ripening may be carried out at ordinary temperatures or at subnormal or raised temperatues, for example, temperatures of 10° C., or less or of 30 or 40° C., or more, according to the reduction in viscosity required and the rate at which it is desired that it should take place. For example oxyethyl cellulose, obtained by oxyalkylating cellulosic material with ethylene chlorhydrin in the presence of caustic soda, may be ripened in a slowly rotating closed vessel into which air is passed at a controlled rate so as to avoid any over-heating of the mass.

Ripening may also be effected by allowing cellulose or other carbohydrate ethers impregnated with an oxidising agent, e.g. potassium permanganate, chlorate or nitrate or hydrogen peroxide, to stand; either in an oxidising or a non-oxidising atmosphere.

The production of the ethers may be effected in any suitable manner, for example by etherifying cellulose, starch, or other carbohydrate materials with ethylene oxide, ethylene chlorhydrin, glycide or monochlorhydrin. The process may also be employed for the reduction of the viscosity of ethers containing ether groups which are free from hydroxy radicles, for example cellulose ethers obtained by etherifying cellulose with dimethyl sulphate, ethyl chloride or benzyl chloride in the presence of caustic alkali. It is, however, particularly valuable in the manufactue of oxyalkyl ethers of cellulose and especially in connection with the oxyalkyl ethers of cellulose obtained by processes described in Specifications Nos. 463,317 and 474,975.

Dated this 5th day of August, 1936.

STEPHENS & ALLEN,
Chartered Patent Agents,
Celanese House, 22 & 23, Hanover Square,
London, W.1.

[Price 1/-]

COMPLETE SPECIFICATION

Improvements in the Manufacture of Ethers of Cellulose and Other Carbohydrates

We, HORACE FINNINGLEY OXLEY, EDWARD BOADEN THOMAS and JOHN DOWNING, all subjects of the King of Great Britain, of the Works of British Celanese Limited, Spondon, near Derby, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to improvements in the manufacture of carbohydrate derivatives, and particularly to improvements in the manufacture of ethers of cellulose and other carbohydrates.

For certain purposes, for example for use in the manufacture of sizes, it is desirable that ethers of cellulose and other carbohydrates, for example starch, should not have too high a viscosity; and in order to produce ethers of the low viscosity required, it has been proposed either to subject the carbohydrate material to partial degradation before etherification, for example by heating it with acids or alkalis, or to carry out the etherification under such conditions as to cause degradation, for example by the use of high temperatures. Both these methods, however, have the disadvantage that it is not possible to be certain that the product eventually obtained will have exactly the desired viscosity.

It has now been discovered that the viscosity of ethers of carbohydrates may be reduced by subjecting the ethers themselves to treatment with an agent containing or yielding free oxygen in the presence of a base, e.g. sodium or potassium hydroxide, tetra-methyl ammonium hydroxide or other strong organic base. This treatment will be referred to in the description as a "ripening" operation. Preferably the ripening is effected by subjecting the ethers in a solid state containing a base to "aeration" with air or other gaseous medium containing or consisting of free oxygen, e.g. by passing the gaseous medium through the ethers or subjecting them to treatment in a closed vessel with the medium under pressure. At ordinary temperatures, particularly at low pressures, e.g. atmospheric pressure, the reduction in viscosity proceeds comparatively slowly, so that it is easy to take samples at suitable intervals and to interrupt the ripening process when a product of the desired degree of viscosity has been obtained. The reduction of the viscosity of the ethers is most suitably effected by means of ordinary air, but if desired oxygen may, as stated above, be employed alone or mixed with vapours, e.g. water vapour, and/or with gases other than nitrogen. The presence of gases which react with bases, for example carbon dioxide, should however be avoided, and when air is employed it is preferably freed from carbon dioxide before it is passed into the vessel containing the ether.

The reduction of viscosity is preferably carried out by ripening an ether which has been obtained by etherification of cellulose in the presence of a base while it is still impregnated with the base and is in a moist condition until the desired degree of viscosity is produced. Ethers produced in the absence of a base for example cellulose ethers obtained by etherifying cellulose with ethylene oxide without a catalyst or in the presence of an acid as catalyst, may be impregnated with a base and then ripened in a moist condition. Ripening may be carried out at ordinary temperatures or at subnormal or raised temperatures, for example temperatures of 10° C. or less or of 25° C., 40° C. or 65° C. or more, according to the reduction in viscosity required and the rate at which it is desired that it should take place. For example oxyethyl cellulose, obtained by oxyalkylating cellulosic material with ethylene chlorhydrin in the presence of caustic soda, may be ripened in a slowly rotating closed vessel into which air is passed at a controlled rate so as to avoid any local over-heating of the mass.

Ripening may be effected at atmospheric pressure or at pressures below or above atmospheric pressure, for example at pressures of 2, 5 or 10 atmospheres or more. In general, increase of temperature and/or of pressure accelerates the ripening. For example, a cellulose ether having originally a viscosity such that a 2% aqueous solution has a specific viscosity as defined below of 27 at 20° C., may require about 100 hours ripening at atmospheric pressure and temperature in order to yield a product giving an aqueous solution having the same specific viscosity when present in a concentration of about 12% and about 200 hours ripening

under the same conditions to yield a product giving a solution of the same specific viscosity when present in a concentration of about 17 to 18%, whereas products of similar viscosities may be obtained from a similar cellulose ether, when ripening at 40 to 50° C. under a pressure of 40 to 50 pounds per square inch, with ripening periods of about 8 hours and 20 hours respectively.

Ripening may for example be continued until a product is obtained which yields an aqueous solution having a specific viscosity as defined below of 20 to 30 when present in a concentration of about 4% or until the product yields an aqueous solution of the above viscosity when present in a concentration of about 15%. The products of higher viscosity are very suitable as thickeners for printing pastes, while the lower viscosity products may be used as sizes.

The specific viscosity of the aqueous solution is given by the formula $\frac{t_1 d}{t_2}$ where

t_1 is the number of seconds required for a given volume of the solution at 20° C. to flow through a given capillary tube;

t_2 is the number of seconds for an equal volume of water at 0° C.;

d is the density of the solution in grams per cubic centimetre.

The production of the ethers may be effected in any suitable manner, for example by etherifying cellulose, starch, or other carbohydrate materials with ethylene oxide, ethylene chlorhydrin, glycide or monochlorhydrin. The process may also be employed for the reduction of the viscosity of ethers containing ether groups which are free from hydroxy radicles, for example cellulose ethers obtained by etherifying cellulose with dimethyl sulphate, ethyl chloride or benzyl chloride in the presence of caustic alkali. It is, however, particularly valuable in the manufacture of oxyalkyl ethers of cellulose and especially in connection with the oxyalkyl ethers of cellulose obtained by processes described in Specifications Nos. 463,317 and 473,975.

Thus, for example, the process of the present invention may be applied to oxyalkyl ethers of cellulose which have been obtained by impregnating cellulose with a 10 to 16% aqueous solution of a base centrifuging, removing water by treatment under reduced pressure as described in Specification No. 473,975 until the proportion of water is about 40 to 50% of the weight of the mass, and then etherifying with ethylene oxide or other suitable oxyalkylating agent, preferably under reduced pressure.

The following Examples illustrate the invention but are not to be regarded as limiting it:—

EXAMPLE 1.

An oxyethyl cellulose in a granular form obtained, for example, by the process described in Specification No. 473,975 which contains about 13% of its weight of sodium hydroxide and about 30% of its weight of water is kept in motion in a rotary vessel at ordinary temperature while a slow current of air free from carbon dioxide is passed through. The progress of the ripening is determined by withdrawing samples from time to time, dissolving them in water, neutralising, for example with hydrochloric acid, and determining the viscosity. When a product of the desired viscosity has been obtained the operation is stopped and the product may be dissolved in water and the solution neutralised, e.g. with acetic or boric acid

EXAMPLE 2.

An oxyethyl cellulose in a granular form is ripened in a manner similar to that described in the previous Example with the exception that the temperature is maintained at 40 to 50° C. and the air pressure is 3 to 4 atmospheres. Under these conditions the rate of ripening is considerably increased, for example it may be 8 to 12 times as rapid.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. Process for reducing the viscosity of ethers of carbohydrates, which comprises subjecting them to treatment with an agent containing or yielding free oxygen in the presence of a base.

2. Process for reducing the viscosity of cellulose ethers, which comprises subjecting them to treatment with an agent containing or yielding free oxygen in the presence of a base.

3. Process according to Claim 1 or 2, wherein the base is sodium or potassium hydroxide.

4. Process according to any of the preceding claims, wherein the ethers are in the solid state.

5. Process according to any of the preceding claims, wherein the ethers which are treated are oxyalkyl ethers.

6. Process according to any of Claims 1 to 4, wherein the ethers which are treated are oxyethyl ethers.

7. Process according to any of the preceding claims, wherein the treatment is effected at a temperature between 25° C. and 65° C.

8. Process according to any of the pre-

ceding claims, wherein the treatment is effected by subjecting an ether containing a base to aeration with a gaseous medium containing or consisting of free oxygen.

9. Process according to Claim 8, wherein the treatment is effected by passing a current of air or other oxygen containing gas through the ether in a granular form.

10. Process according to Claim 8 or 9, wherein the gaseous medium is under super-atmospheric pressure.

11. Process according to Claim 10, wherein the pressure is at least 2 atmospheres.

12. Process according to any of the preceding claims, wherein the ether has been obtained by the etherification of alkali-containing carbohydrate, obtained by impregnating carbohydrate material with an aqueous solution of caustic alkali and concentrating the alkali on the material under reduced pressure until the water-content of the mass is about 40% of the total weight of the mass.

13. Process for reducing the viscosity of ethers of carbohydrates substantially as hereinbefore described.

14. Ethers of cellulose and other carbohydrates when obtained by any of the processes hereinbefore described and claimed, or by their obvious chemical equivalents.

Dated this 28th day of June, 1937.

STEPHENS & ALLEN.
Chartered Patent Agents,
Celanese House, 22 & 23, Hanover Square,
London, W.1.

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